WHAT IS CLAIMED IS:

1. A method of chemically ligating two oligopeptides, wherein a first oligopeptide thioester having an acidic C-terminal amino acid, said acidic C-terminal amino acid having a thioester moiety, a side chain, and a side chain protecting group such that said side chain protecting group substantially prevents rearrangements between atoms of said side chain and atoms of said thioester moiety, is contacted with a second oligopeptide having an N-terminal amino acid under chemical ligation conditions such that said thioester moiety of said first oligopeptide thioester ligates to said N-terminus of said second oligopeptide to form an oligopeptide or polypeptide product.

2. The method of claim 1 wherein said side chain protecting group is selected from the group consisting of 9-fluorenylmethyl ester, (phenylsulfonyl)ethyl ester, 2,2,2-trichloroethyl ester, and a phenacyl ester.

3. The method of claim 2 wherein said side chain protecting group is a phenacyl ester having the formula:

$$-CH(R^{13})-CO-(C_6H_4)-R^{14}$$

wherein R^{13} and R^{14} are each electron-donating groups.

4. The method of claim 3 wherein R^{13} and R^{14} are each alkyl having from 1 to 3 carbon atoms.

5. The method of claim 4 wherein R^{13} is methyl or ethyl.

6. The method of claim 2 wherein said N-terminal amino acid of said second oligopeptide is cysteine or an amino acid with a removable ethylthiol moiety.

7. The method of claim 1 wherein one of said first and second oligopeptide is attached to a solid support.

8. An oligopeptide thioester defined by the formula:

$$Xaa_i- \ldots -Xaa_m-CO-NH-CH[(CH_2)_n-CO-O-R^{12}]-CO-SR^{11}$$

wherein:

each Xaa_i is independently a protected or unprotected amino acid for i=1 to m;

m is an integer from 2 to 70;

n is an integer equal to 1 or 2;

R^{11} is a member selected from the group consisting of alkyl having from 1 to 6 carbon atoms, alkylaryl having from 6 to 8 carbon atoms, $-CH_2-CONH_2$, $-CH_2CH_2CONH_2$, and $-(CH_2)_k-CO-Xaa$, wherein subscript k is an integer equal to 1 or 2 and Xaa is an amino acid; and

R^{12} is a carboxy protecting group.

9. The oligopeptide of claim 8 wherein R^{12} is selected from the group consisting of 9-fluorenylmethyl ester, (phenylsulfonyl)ethyl ester, 2,2,2-trichloroethyl ester, and a phenacyl ester.

10. The oligopeptide of claim 9 wherein R^{12} is a phenacyl ester defined by the formula:

$$-CH(R^{13})-CO-(C_6H_4)-R^{14}$$

wherein R^{13} and R^{14} are each an electron-donating group.

11. The oligopeptide of claim 8 wherein said oligopeptide thioester is attached to a solid support.